

DESALTING METHOD OF SEA WATER BY REFRIGERATION IN DIRECTCONTACT WITH LNG

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Applicant(s):: TOKYO GAS KK; others: 01
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Priority Number(s):
IPC Classification: C02F1/22
EC Classification:
Equivalents:

Abstract

PURPOSE:To desalt sea water efficiently by bringing LNG and sea water into direct contact with each other to produce hydrate, decomposing the same under reduced pressure, converting the same to ice and separating ice from the sea water.

CONSTITUTION:Sea water 11 is pumped 12 into a crystallizing tank 13, where the sea water contacts directly with the LNG15 supplied into the tank by a pump 14. The LNG15 deprives the sea water 11 of heat and is discharged as NG16 from the tank 13. Part of the NG reacts with the sea water 11 and forms hydrate. The slurry consisting of the hydrate and the sea water is transferred into a decomposing tank 17, where the hydrate is decomposed under reduced pressure and is separated to the NG and water. The water is frozen to ice by the heat of decomposition. The decomposition is continued for ≥ 7 min. The slurry consisting of the sea water and the ice is fed into a decomposing tank 18, where the slurry is separated to ice and brine. The ice is washed with part 24A of the fresh water 24 formed in a thawing tank 23 and is then fed into the tank 23.

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⑩ 日本国特許庁 (JP)

⑪ 特許出願公開

⑫ 公開特許公報 (A)

昭58—109179

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C 02 F 1/22

識別記号

庁内整理番号
6685—4D

⑭ 公開 昭和58年(1983)6月29日
発明の数 1
審査請求 未請求

(全 4 頁)

⑮ LNG直接々触冷凍海水淡水化方法

⑯ 特 願 昭56—206983
⑰ 出 願 昭56(1981)12月23日
⑱ 発 明 者 洲上武彦
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会社日立製作所日立研究所内
㉑ 発 明 者 安達哲朗

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⑳ 発 明 者 六串俊巳
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㉑ 発 明 者 江原勝也
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㉒ 出 願 人 東京瓦斯株式会社
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㉓ 代 理 人 弁理士 高橋明夫

最終頁に続く

明 細 書

発明の名称 LNG直接々触冷凍海水淡水化方
法

特許請求の範囲

1. LNGをガス化するLNG気化方法において、
LNGと海水とを直接々触させ、この直接々触に
よつて生成したハイドレートを減圧分解して水に
変換せしめ、しかる後海水からこの水を生離する
と共に融解して淡水化することを特徴とする
LNG直接々触冷凍海水淡水化方法。
2. ハイドレートの減圧分解時間を7分以上とし
たことを特徴とする特許請求の範囲第1項記載の
LNG直接々触冷凍海水淡水化方法。
3. 水の融解に使用した海水をLNGとの直接々
触に使用することを特徴とする特許請求の範囲第
1項記載のLNG直接々触冷凍海水淡水化方法。

発明の詳細な説明

本発明はLNG(液化天然ガス)と海水とを直
接々触させる海水淡水化方法に関する。

近年石油事情の悪化及びクリーンエネルギーへ

の指向からLNGの使用量が年々増加して来てい
る。

LNGは産地にて -160°C に冷却液化され、
消費地に輸送される。消費地では、加熱しガス化
して使用する。LNGは冷熱として約 200Kcal/Kg
を有するため、その有効利用を図ることが消エ
ネルギーの見地から重要視されている。

LNGのガス化方式は従来より(1)オープンラッ
ク式、(2)サブマージ式が採用されて来たが、両方
式ともLNGの持つている冷熱を有効利用するこ
とができない。LNGの冷熱を利用する方法とし
ては冷熱発電、低温倉庫、海水淡水化などが考え
られる。海水淡水化を行なう方法としてはLNG
の冷熱を高沸点の冷媒に移行させ、この冷媒と海
水を直接々触させる方法とLNGと海水とを直接
接触させる方法である。LNGと海水を直接々触
させる方法は、熱交換器がなく、その熱交換特性
は極めて良好となり、LNGの冷熱を海水にうつ
し、LNGをNG(天然ガス)とすることができ
る。この直接々触法のフローを第1図に示す。1

は海水、2は海水ポンプ、4はLNG、5はLNGポンプであり、海水1とLNG4は晶析槽8内において直接々触し、LNG4は海水に冷熱を移しNG3となるものである。この時、LNG4に対する海水1の量を削減して行くことにより、海水中に氷晶とハイドレート（炭化水素の水和物）が生成する。ハイドレートの生成量はLNGの組成、晶析圧力、晶析温度により変化する。なお6はブラインポンプ、7はブラインである。第2図はCH₄ 8.9 mol%のLNGのハイドレートの生成域を示したもので、圧力10 kg/cm² G以上になると、その生成が顕著になつてくる。基礎検討の結果ハイドレートが生成する領域ではハイドレートが氷よりも優先的に生成することが明らかになつている。又、晶析圧力が10 kg/cm² G以下ではハイドレートはほとんど生成せず、氷の生成が優先的であることがわかつた。ハイドレートは第3図(a)(b)に模式的に示したように、炭化水素分子がその周囲を水分子の水素結合によりつつまれているもので、減圧により容易に中心の炭化水素が

ガス化し氷晶へと転換する。ハイドレートは結晶体であるが、LNGと海水との直接々触により生成したハイドレート粒子の大きさは約40 μm程度であるので、固液分離操作が困難でありハイドレートの状態での分離洗浄法は実現性がない。

本発明は上記事情に鑑みなされたもので、LNGと海水とを直接々触して生成するハイドレートを有効に炭水として回収することを目的とするものである。

即ち本発明の特徴は、LNGをガス化するLNG気化方法において、LNGと海水とを直接々触させ、この直接々触によつて生成したハイドレートを減圧分解して氷に変換せしめ、しかる後海水からこの氷を分離すると共に融解して炭水化するLNG直接々触冷凍海水炭水化方法にある。

以下本発明の一実施例を第4図によつて説明する。13は海水ポンプ12で送り込まれた海水11とLNGポンプ14で供給されたLNG15を直接々触する晶析槽、16は気化したNG、17は晶析槽13から排出されたハイドレートを

減圧分解して氷に変換する分解槽、18は海水と氷からなるスラリーを氷とブラインに分離する分離槽、23は氷を海水26と間接々触させて融解する融解槽である。19は分離槽18で分離されたブライン、20はそのブラインポンプ、21はブライン19の一部を晶析槽13に循環する循環水、22はその循環水ポンプ、24は融解槽23で生成した炭水であり、その一部は分離槽18の水を洗浄するための洗浄水24Aとして用いられる。25は融解槽23で生成した炭水24Bを分離槽18に循環させる循環ポンプ、27は炭水ポンプ、28は冷海水、29は洗浄水ポンプである。

さて、海水11は海水ポンプ12により晶析槽13に送り込まれ、LNGポンプ14により供給されたLNG15と直接々触する。LNG15は海水11の熱を奪い、NG16となり、晶析槽13から排出されるが、NGの一部は海水11と反応してハイドレートが生成する。海水とハイドレートからなるスラリーは、晶析槽13から分解槽17へと移送される。分解槽17でハイドレ-

ートは減圧分解され、NG16と水分に分かれるが、分解熱により、水は氷に変換する。この時分解時間を10分以上とする。次に、海水と氷からなるスラリーは分解槽16から分離槽18へ移送され、分離槽18ではスラリーは氷とブライン19に分離される。ブライン19はブラインポンプ20により排出されるが、一部は循環水21として循環ポンプ22により晶析槽13に送られる。分離槽18で分離された氷は融解槽23で生成した炭水24の一部24Aで洗浄した後、融解槽23から炭水24Bを循環ポンプ25により循環させて氷を融解槽23に移送する。融解槽23では海水26を間接々触させ氷を融解し、炭水24を生成する。炭水24は炭水ポンプ27により利用施設へ供給される。氷の融解に使用された海水26は冷海水28になり、晶析槽13に投入する海水の1部として利用され、冷熱の有効利用度を高めている。

本発明は前述した如く、ハイドレートを減圧分解し氷晶へと転換し、氷晶をブラインから分離し、

洗淨し炭水を回収するものであるが、第3図に示したように、急激なる減圧分解を行なつた場合、生成する氷晶の粒径もハイドレートの粒径と近いものとなり、ブラインからの分離性能の向上はのぞめない。第5図は晶析圧力から常圧にまで減圧する時間とその時生成した氷晶の粒径を示した。分解時間が短い時は、粒径が細かいが、分解時間を長くすることにより生成する氷晶粒径を大きくすることが可能である。

10分以上では氷の粒径の大きさはほぼ一定に近づく。分解時間7分で飽和値の75%程度まで粒径が増大する。そのため7分以上あれば十分と考えられる。

本発明によれば、LNGと海水とを直接々融して生成するハイドレートを有効に炭水として回収することができる。

図面の簡単な説明

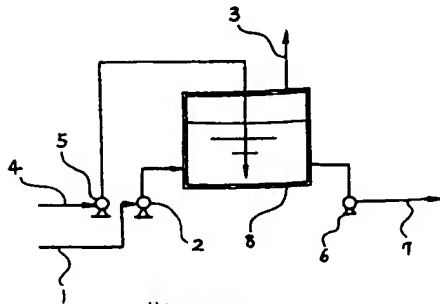
第1図はLNGと海水の直接々融の熱交を示す説明図、第2図はハイドレートの生成域を示す線図、第3図はハイドレートの模式図、第4図は本

発明の一実施例を示すブロック図、第5図は晶析圧力から常圧まで減圧分解と氷晶の粒径の関係を示す線図である。

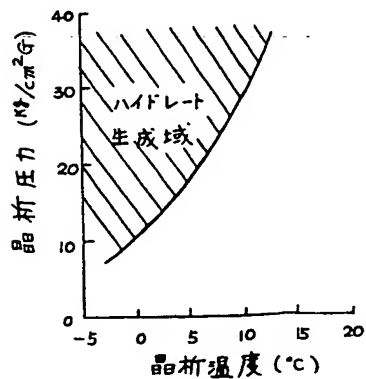
11…海水、15…LNG、9…晶析槽、17…分解槽、18…分離槽、23…融解槽、24…炭水、28…冷海水。

代理人 弁理士 高橋明夫

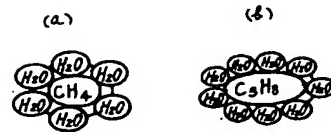
第1図



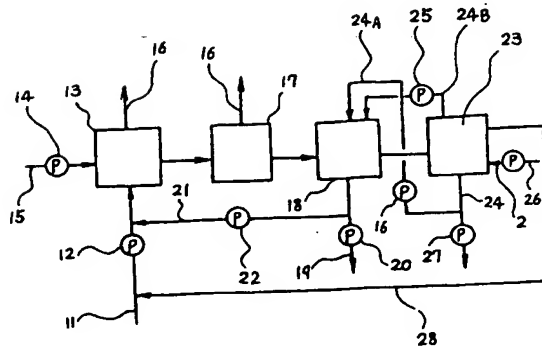
第2図



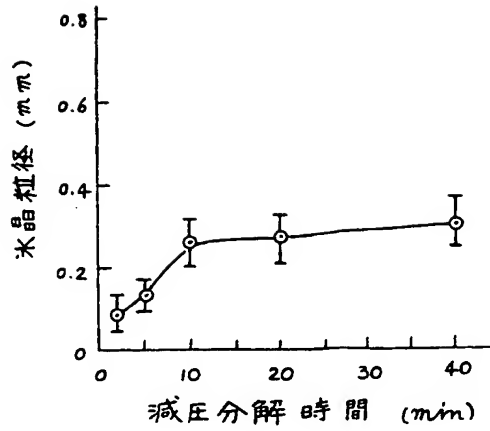
第3図



第4図



第5図



第1頁の続き

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⑨ 日本国特許庁 (JP)
⑩ 公開特許公報 (A)

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昭58—109179

⑫ Int. Cl.³
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発明の数 1
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⑭ LNG直接々触冷凍海水淡水化方法

⑯ 特 願 昭56—206983
⑰ 出 願 昭56(1981)12月23日
⑱ 発 明 者 淵上武彦
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⑲ 発 明 者 二階堂信夫
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明 細 書

発明の名称 LNG直接々触冷凍海水淡水化方法

特許請求の範囲

1. LNGをガス化するLNG気化方法において、LNGと海水とを直接々触させ、この直接々触によつて生成したハイドレートを減圧分解して氷に変換せしめ、しかる後海水からこの氷を分離すると共に融解して淡水化することを特徴とするLNG直接々触冷凍海水淡水化方法。
2. ハイドレートの減圧分解時間を7分以上としたことを特徴とする特許請求の範囲第1項記載のLNG直接々触冷凍海水淡水化方法。
3. 氷の融解に使用した海水をLNGとの直接々触に使用することを特徴とする特許請求の範囲第1項記載のLNG直接々触冷凍海水淡水化方法。

発明の詳細な説明

本発明はLNG(液化天然ガス)と海水とを直接々触させる海水淡水化方法に関する。

近年石油事情の悪化及びクリーンエネルギーへ

の指向からLNGの使用量が年々増加して来ている。

LNGは産地にて -160°C に冷却液化され、消費地に輸送される。消費地では、加熱しガス化して使用する。LNGは冷熱として約200Kcal/kgを有するため、その有効利用を図ることが消エネルギーの見地から重視されている。

LNGのガス化方式は従来より(1)オープンラック式、(2)サブマーシジ式が採用されて来たが、両方式ともLNGの持っている冷熱を有効利用することができない。LNGの冷熱を利用する方法としては冷熱発電、低温倉庫、海水淡水化などが考えられる。海水淡水化を行なう方法としてはLNGの冷熱を高沸点の冷媒に移行させ、この冷媒と海水を直接々触させる方法とLNGと海水とを直接々触させる方法とがある。LNGと海水を直接々触させる方法は、熱交換効率がなく、その熱交換特性は極めて良好となり、LNGの冷熱を海水にうつし、LNGをNGI(天然ガス)とすることができ、この直接々触法のフローを第1図に示す。1

沈降し炭水を回収するものであるが、第3図に示したように、急激なる減圧分解を行なった場合、生成する氷晶の粒径もハイドレートの粒径と近いものとなり、ブラインからの分離性能の向上はのぞめない。第5図は晶析圧力から常圧にまで減圧する時間とその時生成した氷晶の粒径を示した。分解時間が短い時は、粒径が細かいが、分解時間を長くすることにより生成する氷晶粒径を大きくすることが可能である。

10分以上では氷の粒径の大きさはほぼ一定に近づく。分解時間7分で飽和値の75%程度まで粒径が増大する。そのため7分以上あれば十分と考えられる。

本発明によれば、LNGと海水とを直接々触して生成するハイドレートを有効に炭水として回収することができる。

図面の簡単な説明

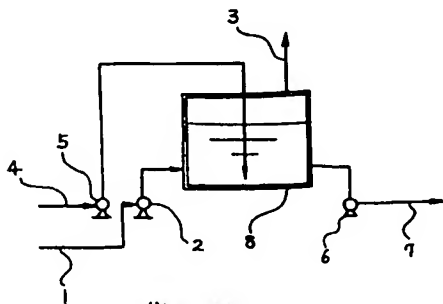
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発明の一実施例を示すブロック図、第5図は晶析圧力から常圧にまで減圧分解と氷晶の粒径の関係を示す線図である。

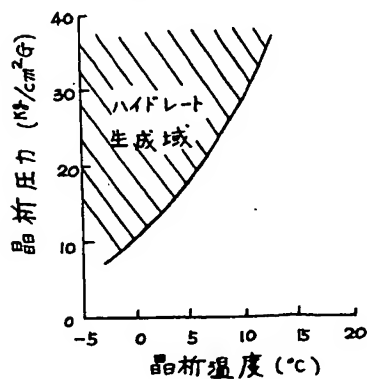
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代理人 弁理士 高橋明夫

第1図



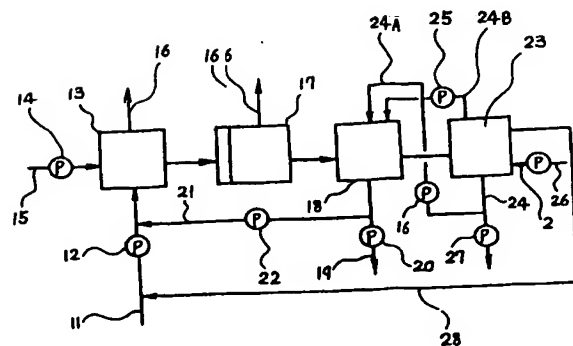
第2図



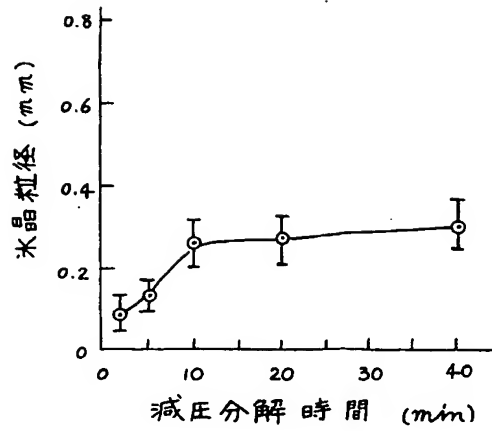
第3図



第4図



第5図



第1頁の続き

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[Page 435, upper half of the page]

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(12) Laid-Open Patent Gazette (A)

(11) Patent Application Laid-Open: Sho 58-109179

(51) Int. Cl.³ Identification Codes Office Reference No. (43) Laid-Open Date: June 29,
Showa 58 (1983)

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Number of Inventions: 1

Request for Examination: Yet to be
made

(4 pages in total)

(54) LNG direct contact frozen seawater desalination method

(21) Patent Application No.: Sho 56-206983

(22) Date of Patent Application: December 23, Showa 56 (1981)

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(74) Agent: Patent Attorney [Benrishi] Akio Takahashi

To be continued onto the last page.

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[Page 435, left-hand column]

Specification

Title of the Invention: LNG direct contact frozen seawater desalination method

Claims:

1. In an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method characterized by allowing LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated.
2. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the duration of hydrate decomposition under reduced pressure being 7 minutes or longer.
3. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the seawater used for the ice to melt being used for the direct contact with the LNG.

Detailed Description of the Invention:

The present invention relates to a seawater desalination method whereby LNG (liquified natural gas) and seawater are brought into direct contact.

In recent years due to the worsening petroleum situation and the direction towards clean energy the amount of LNG used has been on the rise over the years.

[Page 435, right-hand column]

LNG is cooled and liquified in the production region and transported to the region where it is consumed. In the region where it is consumed it is heated and gasified to be used. Since LNG possesses about 200 Kcal/kg as cold heat, what is regarded important from the standpoint of energy-saving [the Chinese character in the Japanese text the translator translated as Asaving@ here is not a character ordinarily used in a phrase Aenergy-saving@ but a Chinese character for Aerase, eliminate, etc.,@ with the same vocalization. Thus the translator believes the Chinese character intended here was that for Asave@ and not Aerase@ judged from the context.] is to work out an effective utilization thereof.

While (1) open rack method and (2) submerge method have conventionally been employed as a method of gasifying LNG, neither method can effectively utilize cold heat LNG possesses. As a method of utilizing LNG=s cold heat, cold heat power generation, low-temperature storage, seawater desalination, etc., can be considered. Methods of desalinating seawater are a method whereby LNG=s cold heat is transferred to a refrigerant with a high boiling point and this refrigerant and seawater are placed in direct contact and a method whereby LNG and seawater are placed in direct contact. There is no heat exchanger with the method whereby LNG and seawater are placed in direct contact, the heat exchange property thereof being extremely good, being capable of transferring the cold heat of LNG to seawater and of making LNG into NG (natural gas). The flow of this direct contact method is illustrated in Fig. 1.

[Page 436, upper left-hand column]

1 refers to seawater, 2 to a seawater pump, 4 to LNG, and 5 to an LNG pump, and seawater 1 and LNG 4 are brought in direct contact in a crystallization tank 8, LNG 4 transferring cold heat to the seawater to become NG 3. At that time, as the volume of seawater 1 is reduced with respect to LNG 4, ice crystals and a hydrate (hydrocarbon hydrate) are formed in the seawater. The amount of hydrate formed varies depending on the composition of LNG, crystallization pressure,

and crystallization temperature. In addition, 6 refers to a brine pump, and 7 to brine. Fig. 2 indicates the formation region of LNG hydrate of CH_4 89 mol%, and when the pressure is 10 Kg/cm^2 G or greater, the generation thereof begins to be marked. The result of the basic study has shown that the formation of hydrate takes precedence over that of ice in the region wherein hydrate is formed. And, we learned that hydrate is hardly formed when the crystallization pressure is 10 kg/cm^2 G or less and that the generation of ice takes precedence. Hydrate is, as illustratively shown in Figs. 3 (a) and (b), a hydrocarbon molecule surrounded with water molecules around it through hydrogen bonding, and is converted into an ice crystal as the hydrocarbon at the center is easily gasified under reduced pressure.

[Page 436, upper right-hand column]

While hydrate is in a crystal form, it is difficult to separate solid from liquid since the size of hydrate particles formed by the direct contact of LNG and seawater is on the order of about 40 Φm , and there is no possibility of the method of separating and washing them in the state of hydrate becoming a reality.

The present invention was made with the above-described situation in view, and aims at effectively recovering as fresh water hydrate formed by LNG and seawater being brought into direct contact.

Namely, the characteristic of the present invention lies with, in an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method which allows LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated

In the following one example of the present invention will be described on the basis of Fig. 4. 13 refers to a crystallization tank wherein seawater 11 fed in by a seawater pump 12 and LNG 15 supplied by an LNG pump 14 are brought into direct contact, 16 to vaporized NG, 17 to the decomposition tank wherein the hydrate discharged from the crystallization tank 13 is decomposed under reduced pressure and converted into ice,

[Page 436, lower left-hand column]

18 to a dissociation tank dissociating the slurry composed of seawater and ice into ice and brine, and 23 to a melting tank wherein ice and seawater 26 are brought into an indirect contact and melted. 19 refers to the brine dissociated in the dissociation tank 18, 20 to the brine pump therefor, 21 to the circulation water circulating a portion of brine 19 back to the crystallization tank 13, 22 to the circulation pump therefor, and 24 to the fresh water formed in the melting tank 23, a portion of which is used as washing water 24A to wash the ice in the dissociation tank 18. 25 refers to the circulation pump circulating the fresh water 24B formed in the melting tank 23 back to the dissociation tank 18, 27 to a fresh water pump, 28 to cold seawater, and 29 to a washing water pump.

Now, seawater 11 is fed into the crystallization tank 13 by the seawater pump 12 and comes into direct contact with LNG 15 supplied by LNG pump 14. LNG 15 robs heat off seawater 11 to become NG 16 and discharged from the crystallization tank 13, and a portion of the NG reacts with seawater 11 to form a hydrate. The slurry composed of seawater and hydrate is transferred from the crystallization tank 13 to the decomposition tank 17.

[Page 436, lower right-hand column]

While the hydrate decomposes in the decomposition tank 17 under reduced pressure and dissociates into NG 16 and the water content, due to decomposition heat water converts into ice. The decomposition time then is to be 10 minutes or longer. Next, the slurry composed of seawater and ice is transferred from the decomposition tank 16 to the dissociation tank 18, and in the dissociation tank 18 the slurry dissociates into ice and brine 19. While brine 19 is discharged with the brine pump 20, a portion thereof is returned to the crystallization tank 13 as circulation water 21 with the circulation pump 22. The ice dissociated in the dissociation tank 18 is, after being washed with a portion 24A of fresh water 24 formed in the melting tank 23, transferred to the melting tank 23 as the fresh water 24B is circulated from the melting tank 23 with the circulation pump 25. In melting tank 23, ice is melted by the seawater 26 being brought into indirect contact to form fresh water 24. Fresh water 24 is supplied to the utilization facility by the fresh water pump 27. Seawater 26 used to melt ice becomes cold seawater 28 and utilized as part of the seawater introduced into the crystallization tank 13 to enhance the degree of effective utilization of cold heat.

While the present invention is, as previously described, to decompose hydrate under reduced pressure to be converted into ice crystals, to dissociate ice crystals from brine and to wash [them] and recover fresh water,

[Page 437, upper left-hand column]

the particle diameter of the ice crystal formed when the decomposition is rapidly performed under reduced pressure results in being close to the particle diameter of the hydrate, as shown in Fig. 3, and an enhanced dissociation performance from brine cannot be anticipated. Fig. 5 illustrates the duration of pressure reduction from crystallization pressure to ambient pressure and the particle diameters of ice crystals formed then. While the particle diameter is small when the decomposition time is short, it is possible to increase by lengthening decomposition time the ice crystal particle diameter formed.

For [the decomposition time of] 10 minutes or longer, the size of the particle diameter thereof reaches to a nearly constant [value]. At the decomposition time 7 minutes the particle diameter increases to about 75% of the saturation value. Accordingly, it is thought that 7 minutes or longer would be sufficient.

According to the present invention, the hydrate formed by LNG and seawater being brought into direct contact can be effectively recovered as fresh water.

Brief Description of the Drawings:

Fig. 1 is a descriptive diagram illustrating the heat exchange of LNG and seawater in direct contact, Fig. 2 a line graph illustrating the region of hydrate formed, Fig. 3 graphical drawings of hydrate,

[Page 437, upper right-hand column]

Fig. 4 a block diagram illustrating an example of the present invention, and Fig. 5 a line graph illustrating the relation between the decomposition under reduced pressure from crystallization pressure to ambient pressure and the particle diameters of the ice crystals.

11.....Seawater, 15.....LNG, 9.....Crystallization tank, 17.....Decomposition tank,

18.....Dissociation tank, 23.....Melting tank, 24.....Fresh water, 28.....Cold seawater.

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[Lower portion of the page]

Fig. 1

[Drawing]

Fig. 3

(a)

[Drawing]

(b)

[Drawing]

Fig. 2

[Graph]
[Label for Y axis]
Crystallization pressure
[Label for X axis]
Crystallization temperature
[Label for the area with oblique lines between the axes]
Hydrate formation region

Fig. 4

[Drawing]

[Page 438, upper left-hand portion of the page]

[Graph]
[Label for Y axis]
Ice crystal particle diameter
[Label for X axis]
Reduced pressure decomposition time

[Page 438, upper right-hand portion of the page]

Continued from page 1.

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(54) LNG direct contact frozen seawater desalination method

(21) Patent Application No.: Sho 56-206983

(22) Date of Patent Application: December 23, Showa 56 (1981)

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Specification

Title of the Invention: LNG direct contact frozen seawater desalination method

Claims:

1. In an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method characterized by allowing LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated.
2. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the duration of hydrate decomposition under reduced pressure being 7 minutes or longer.
3. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the seawater used for the ice to melt being used for the direct contact with the LNG.

Detailed Description of the Invention:

The present invention relates to a seawater desalination method whereby LNG (liquified natural gas) and seawater are brought into direct contact.

In recent years due to the worsening petroleum situation and the direction towards clean energy the amount of LNG used has been on the rise over the years.

[Page 435, right-hand column]

LNG is cooled and liquified in the production region and transported to the region where it is consumed. In the region where it is consumed it is heated and gasified to be used. Since LNG possesses about 200 Kcal/kg as cold heat, what is regarded important from the standpoint of energy-saving [the Chinese character in the Japanese text the translator translated as Asaving@ here is not a character ordinarily used in a phrase Aenergy-saving@ but a Chinese character for Aerase, eliminate, etc.,@ with the same vocalization. Thus the translator believes the Chinese character intended here was that for Asave@ and not Aerase@ judged from the context.] is to work out an effective utilization thereof.

While (1) open rack method and (2) submerge method have conventionally been employed as a method of gasifying LNG, neither method can effectively utilize cold heat LNG possesses. As a method of utilizing LNG=s cold heat, cold heat power generation, low-temperature storage, seawater desalination, etc., can be considered. Methods of desalinating seawater are a method whereby LNG=s cold heat is transferred to a refrigerant with a high boiling point and this refrigerant and seawater are placed in direct contact and a method whereby LNG and seawater are placed in direct contact. There is no heat exchanger with the method whereby LNG and seawater are placed in direct contact, the heat exchange property thereof being extremely good, being capable of transferring the cold heat of LNG to seawater and of making LNG into NG (natural gas). The flow of this direct contact method is illustrated in Fig. 1.

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1 refers to seawater, 2 to a seawater pump, 4 to LNG, and 5 to an LNG pump, and seawater 1 and LNG 4 are brought in direct contact in a crystallization tank 8, LNG 4 transferring cold heat to the seawater to become NG 3. At that time, as the volume of seawater 1 is reduced with respect to LNG 4, ice crystals and a hydrate (hydrocarbon hydrate) are formed in the seawater. The amount of hydrate formed varies depending on the composition of LNG, crystallization pressure,

and crystallization temperature. In addition, 6 refers to a brine pump, and 7 to brine. Fig. 2 indicates the formation region of LNG hydrate of CH_4 89 mol%, and when the pressure is 10 Kg/cm^2 G or greater, the generation thereof begins to be marked. The result of the basic study has shown that the formation of hydrate takes precedence over that of ice in the region wherein hydrate is formed. And, we learned that hydrate is hardly formed when the crystallization pressure is 10 kg/cm^2 G or less and that the generation of ice takes precedence. Hydrate is, as illustratively shown in Figs. 3 (a) and (b), a hydrocarbon molecule surrounded with water molecules around it through hydrogen bonding, and is converted into an ice crystal as the hydrocarbon at the center is easily gasified under reduced pressure.

[Page 436, upper right-hand column]

While hydrate is in a crystal form, it is difficult to separate solid from liquid since the size of hydrate particles formed by the direct contact of LNG and seawater is on the order of about 40 Φm , and there is no possibility of the method of separating and washing them in the state of hydrate becoming a reality.

The present invention was made with the above-described situation in view, and aims at effectively recovering as fresh water hydrate formed by LNG and seawater being brought into direct contact.

Namely, the characteristic of the present invention lies with, in an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method which allows LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated

In the following one example of the present invention will be described on the basis of Fig. 4. 13 refers to a crystallization tank wherein seawater 11 fed in by a seawater pump 12 and LNG 15 supplied by an LNG pump 14 are brought into direct contact, 16 to vaporized NG, 17 to the decomposition tank wherein the hydrate discharged from the crystallization tank 13 is decomposed under reduced pressure and converted into ice,

[Page 436, lower left-hand column]

18 to a dissociation tank dissociating the slurry composed of seawater and ice into ice and brine, and 23 to a melting tank wherein ice and seawater 26 are brought into an indirect contact and melted. 19 refers to the brine dissociated in the dissociation tank 18, 20 to the brine pump therefor, 21 to the circulation water circulating a portion of brine 19 back to the crystallization tank 13, 22 to the circulation pump therefor, and 24 to the fresh water formed in the melting tank 23, a portion of which is used as washing water 24A to wash the ice in the dissociation tank 18. 25 refers to the circulation pump circulating the fresh water 24B formed in the melting tank 23 back to the dissociation tank 18, 27 to a fresh water pump, 28 to cold seawater, and 29 to a washing water pump.

Now, seawater 11 is fed into the crystallization tank 13 by the seawater pump 12 and comes into direct contact with LNG 15 supplied by LNG pump 14. LNG 15 robs heat off seawater 11 to become NG 16 and discharged from the crystallization tank 13, and a portion of the NG reacts with seawater 11 to form a hydrate. The slurry composed of seawater and hydrate is transferred from the crystallization tank 13 to the decomposition tank 17.

[Page 436, lower right-hand column]

While the hydrate decomposes in the decomposition tank 17 under reduced pressure and dissociates into NG 16 and the water content, due to decomposition heat water converts into ice. The decomposition time then is to be 10 minutes or longer. Next, the slurry composed of seawater and ice is transferred from the decomposition tank 16 to the dissociation tank 18, and in the dissociation tank 18 the slurry dissociates into ice and brine 19. While brine 19 is discharged with the brine pump 20, a portion thereof is returned to the crystallization tank 13 as circulation water 21 with the circulation pump 22. The ice dissociated in the dissociation tank 18 is, after being washed with a portion 24A of fresh water 24 formed in the melting tank 23, transferred to the melting tank 23 as the fresh water 24B is circulated from the melting tank 23 with the circulation pump 25. In melting tank 23, ice is melted by the seawater 26 being brought into indirect contact to form fresh water 24. Fresh water 24 is supplied to the utilization facility by the fresh water pump 27. Seawater 26 used to melt ice becomes cold seawater 28 and utilized as part of the seawater introduced into the crystallization tank 13 to enhance the degree of effective utilization of cold heat.

While the present invention is, as previously described, to decompose hydrate under reduced pressure to be converted into ice crystals, to dissociate ice crystals from brine and to wash [them] and recover fresh water,

[Page 437, upper left-hand column]

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For [the decomposition time of] 10 minutes or longer, the size of the particle diameter thereof reaches to a nearly constant [value]. At the decomposition time 7 minutes the particle diameter increases to about 75% of the saturation value. Accordingly, it is thought that 7 minutes or longer would be sufficient.

According to the present invention, the hydrate formed by LNG and seawater being brought into direct contact can be effectively recovered as fresh water.

Brief Description of the Drawings:

Fig. 1 is a descriptive diagram illustrating the heat exchange of LNG and seawater in direct contact, Fig. 2 a line graph illustrating the region of hydrate formed, Fig. 3 graphical drawings of hydrate,

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Fig. 4 a block diagram illustrating an example of the present invention, and Fig. 5 a line graph illustrating the relation between the decomposition under reduced pressure from crystallization pressure to ambient pressure and the particle diameters of the ice crystals.

11.....Seawater, 15.....LNG, 9.....Crystallization tank, 17.....Decomposition tank,

18.....Dissociation tank, 23.....Melting tank, 24.....Fresh water, 28.....Cold seawater.

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[Lower portion of the page]
Fig. 1

Fig. 3

(a)

(b)

[Drawing]

[Drawing]

[Drawing]

Fig. 2

Fig. 4

[Graph]

[Drawing]

[Label for Y axis]

Crystallization pressure

[Label for X axis]

Crystallization temperature

[Label for the area with oblique lines between the axes]

Hydrate formation region

[Page 438, upper left-hand portion of the page]

[Graph]

[Label for Y axis]

Ice crystal particle diameter

[Label for X axis]

Reduced pressure decomposition time

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